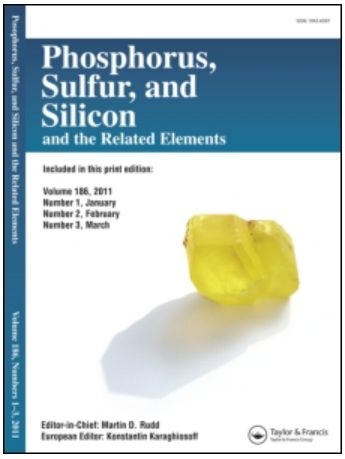

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SYNTHESIS AND CONFIGURATIONAL STUDIES OF ARYL CYCLOPROPYL SULFONES

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SYNTHESIS AND CONFIGURATIONAL STUDIES OF ARYL CYCLOPROPYL SULFONES

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The cycloaddition of arylthiocarbenes to styrene gave stereospecifically *cis*-1-(arylthio)-2-phenylcyclopropanes, which were subsequently oxidized to the corresponding sulfones. The cyclopropanation of α,β-unsaturated sulfones with dimethylsulfonium methylide yielded stereoselectively *trans*-1-(arylsulfonyl)-2-arylcyclopropanes. The configurational assignments of these compounds have been arrived at on the basis of IR and PMR spectral data. Chemical shifts for ring protons and other substituents reveal that all the substituents tend to cause protons *cis* to them to appear at higher fields than those *trans* to them. This has been used as a criterion to distinguish between *cis* and *trans* aryl cyclopropyl sulfones.

INTRODUCTION

Although several methods are known for the synthesis of cyclopropanes for a long time, the first cyclopropyl sulfone was reported only in 1960 by Zimmerman and Thyagarajan.[1] Later a number of methods were reported for the synthesis of cyclopropyl sulfones.[2-6] Inspite of all the available methods for the synthesis of aryl cyclopropyl sulfones, the cycloaddition of carbenes to carbon–carbon multiple bonds and the utility of sulfur ylides with Michael acceptors seem to be more important and synthetic value.

Carbenes are among the most versatile as well as synthetically useful organic reactive intermediates. The addition of singlet carbenes to carbon–carbon multiple bonds presents a highly general approach for the synthesis of cyclopropanes and is always stereospecifically *cis* with olefinic double bonds.[7] Schoellkopf *et al.*,[2,8,9] reported the cyclopropanation of the olefins with chloromethyl phenyl ether ($PhOCH_2Cl$) and chloromethyl phenyl sulfide ($PhSCH_2Cl$) through phenoxycarbene and phenylthiocarbene intermediates respectively. Several carbene intermediates have also been reported[10] for the cycloaddition of alkenes in a stereospecific manner.

The usefulness of ylides in organic synthesis was better realized with the introduction of the Wittig olefin synthesis. Sulfur ylides, formally Zwitter ions, are nucleophilic alkylidene transfer agents and react with electron deficient functional groups. The general synthetic utility of dimethylsulfoxonium methylide (I) and dimethylsulfonium methylide (II) as reagents for the addition of methylene to double bonds, which are receptive to nucleophiles has been studied by Corey and

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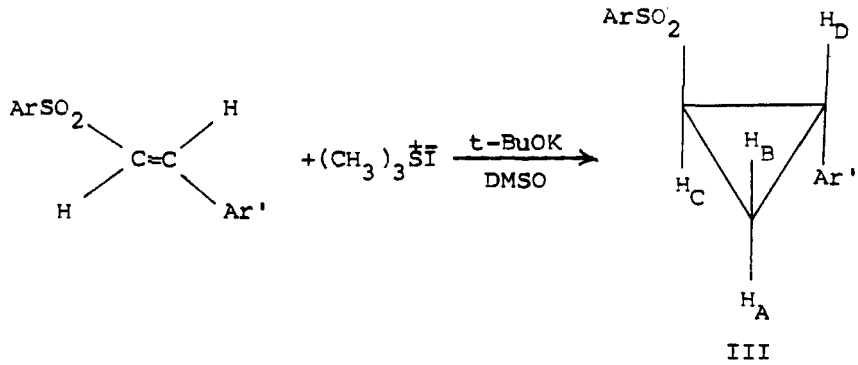
Chaykovsky.[11] A wide variety of the sulfur ylides have been explored for the cyclopropanation of Michael acceptors by different workers.[12] The reaction of ylide (II) with trans α,β-unsaturated esters, nitriles, amides and conjugated nitro olefins were reported to yield stereoselectively *trans*-cyclopropyl derivatives.[12]

Although the synthesis and study of quite a few *trans*-aryl cyclopropyl sulfones are known,[13,14] there are sparse reports about the synthesis and study of the corresponding *cis*-compounds in the literature.[13] Hence we wish to report here, the synthesis of some *cis* and *trans*-aryl cyclopropyl sulfones, by the cycloaddition of arylthiocarbenes to styrene and the ylide (II), to α,β-unsaturated sulfones. Their configurational assignments have also been studied.

RESULTS AND DISCUSSION

Truce and Badiger[13] first reported the synthesis of *cis* and *trans*-1-(phenylsulfonyl)-2-phenylcyclopropane. The utility of ylide (II) as a co-reactant with α,β-unsaturated sulfones seems to lie in its stereoselectivity and the cyclopropyl sulfones thus obtained were considered to have *trans*-configuration.[13–15]

A series of new *trans*-1-(arylsulphonyl)-2-arylcyclopropanes (III) (see Table I) were prepared by treating α,β-unsaturated sulfones with trimethylsulfonium iodide in the presence of potassium *t*-butoxide in dry dimethyl sulfoxide under anhydrous conditions.



III

A few new *cis*-1-(arylsulphonyl)-2-phenylcyclopropanes were synthesized by the cycloaddition of aryl chloromethyl sulfides to excess of styrene in the presence of potassium *t*-butoxide at low temperatures. The *cis*-1-(arylthio)-2-phenylcyclopropanes (IV) (see Table II) thus formed were oxidized subsequently with 30% hydrogen peroxide in glacial acetic acid to result *cis*-1-(arylsulfonyl)-2-phenylcyclopropanes (V) (see Table III) in fairly high yields.

The IR spectra (ν_{max} in cm^{-1}) of these compounds showed medium to strong intensity bands in the region 1044–1022, characteristic of the cyclopropane deformation mode of the ring[16,17] (see Tables I and III). Two bands in the regions 3085–3060 (ν_{as} CH_2) and 3025–3000 (ν_s CH_2), in addition to the former bands confirms the presence of cyclopropane ring system. They also exhibited bands of varying intensi-

TABLE I

trans-1-(Arylsulfonyl)-2-arylcyclopropanes—III

S. No.	Ar	Ar′	Yield %	mp °C	Mol. formula	Analyses % Calcd. C	Calcd. H	Found C	Found H	IR (KBr) ν (cm^{-1}) Ring deformation 1026 region	Absorption band at 1100 region	Absorption band at 910 region
1	4-BrC_6H_4	4-$CH_3OC_6H_4$	86.2	131–132	$C_{16}H_{15}BrO_3S$	52.31	4.12	52.48	4.16	1040	1100	920
2	2-ClC_6H_4	H	72.5	110–111	$C_{15}H_{13}ClO_2S$	61.55	4.47	61.58	4.56	1032	1103	920
3	4-ClC_6H_4	3-ClC_6H_4	74.8	102–103	$C_{15}H_{12}Cl_2O_2S$	55.00	3.70	54.90	3.80	1030	1115	925
4	4-$CH_3OC_6H_4$	H	80.0	126–127	$C_{16}H_{16}O_3S$	66.64	5.59	66.55	5.48	1020	1108	918
5	4-$CH_3C_6H_4$	2,5-$(CH_3O)_2C_6H_3$	70.8	110–111	$C_{18}H_{20}O_4S$	65.03	6.06	64.83	5.96	1027	1105	924
6	4-Cl-3-$CH_3C_6H_3$	H	70.6	101–102	$C_{16}H_{15}ClO_2S$	62.65	4.93	63.03	4.98	1043	1110	915

TABLE II

cis-1-(Arylthio)-2-phenylcyclopropanes—IV

S. No.	Ar	Yield %	bp °C/mm or mp °C	Mol. formula	Analyses % Calcd. C	Calcd. H	Found C	Found H	IR (KBr) ν (cm^{-1}) Ring deformation 1026 region	IR (KBr) ν (cm^{-1}) *S*-Aryl 1090 region
1	4-BrC_6H_4	61.0	200/10	$C_{15}H_{13}BrS$	59.93	4.29	59.72	4.08	1028	1090
2	2-ClC_6H_4	63.0	182/12	$C_{15}H_{13}ClS$	69.08	5.02	68.91	4.91	1032	1078
3	4-ClC_6H_4	59.0	191/10	$C_{15}H_{13}ClS$	69.08	5.02	68.89	4.84	1028	1089
4	4-$CH_3OC_6H_4$	66.0	175/8	$C_{16}H_{16}OS$	74.96	6.29	74.75	6.18	1020	1080
5	3-$CH_3C_6H_4$	55.0	212/12	$C_{16}H_{16}S$	79.95	6.71	80.14	6.75	1026	1095
6	4-$CH_3C_6H_4$	61.0	210/10	$C_{16}H_{16}S$	79.95	6.71	79.91	6.63	1027	1088
7	2-$NO_2C_6H_4$	64.0	53–54	$C_{15}H_{13}NO_2S$	55.27	4.87	55.01	4.99	1038	1080
8	4-$NO_2C_6H_4$	65.0	64–65	$C_{15}H_{13}NO_2S$	55.27	4.87	55.50	5.00	1038	1098
9	3,4-$Cl_2C_6H_3$	60.4	219/9	$C_{15}H_{12}Cl_2S$	50.84	4.10	51.02	4.23	1030	1088
10	4-Cl-3-$CH_3C_6H_3$	58.6	231/12	$C_{16}H_{15}ClS$	70.65	5.56	70.43	5.49	1040	1098
11	5-Cl-2-$CH_3C_6H_3$	61.8	218/12	$C_{16}H_{15}ClS$	70.65	5.56	70.41	5.59	1030	1105
12	$C_6H_5CH_2$	53.3	209/14	$C_{16}H_{16}S$	79.95	6.71	79.74	6.56	1028	1100

TABLE III

cis-1-(Arylsulfonyl)-2-phenylcyclopropanes—V

S. No.	Ar	Yield %	mp °C	Mol. formula	Analyses % Calcd. C	Calcd. H	Found C	Found H	IR (KBr) ν (cm^{-1}) Ring deformation 1026 region	IR (KBr) ν (cm^{-1}) Absorption band at 848 region
1	4-BrC_6H_4	80.8	109–110	$C_{15}H_{13}BrO_2S$	53.41	3.88	53.26	3.82	1030	840
2	2-ClC_6H_4	76.6	101–102	$C_{15}H_{13}ClO_2S$	61.53	4.47	61.30	4.38	1030	838
3	4-ClC_6H_4	78.6	90–91	$C_{15}H_{13}ClO_2S$	61.53	4.47	61.40	4.58	1035	836
4	4-$CH_3OC_6H_4$	86.4	114–115	$C_{16}H_{16}O_3S$	66.64	5.59	66.59	5.59	1025	845
5	3-$CH_3C_6H_4$	80.7	94–95	$C_{16}H_{16}O_2S$	70.36	5.92	70.56	5.99	1030	835
6	2-$NO_2C_6H_4$	81.7	143–144	$C_{15}H_{13}NO_4S$	59.39	4.33	59.06	4.39	1028	848
7	4-Cl-3-$CH_3C_6H_3$	81.5	116–117	$C_{16}H_{15}ClO_2S$	62.65	4.93	62.45	5.07	1040	832
8	5-Cl-2-$CH_3C_6H_3$	83.5	160–161	$C_{16}H_{13}ClO_2S$	62.65	4.93	63.02	5.05	1030	835
9	$C_6H_5CH_2$	75.0	102–103	$C_{16}H_{16}O_2S$	70.36	5.92	70.74	6.02	1022	836

TABLE IV

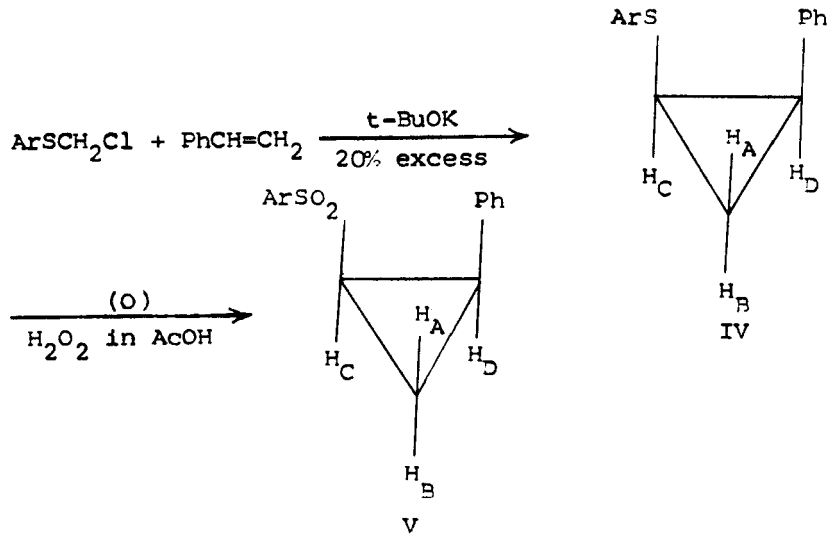
Proton magnetic resonance spectra of *trans*-1-(arylsulfonyl)-2-arylcyclopropanes—III

S. No.	Ar	Ar′	Cyclopropyl (δ, ppm)		Aryl and arylsulfonyl δ, ppm
			CH_2	CH	
1	$4\text{-}BrC_6H_4$	$4\text{-}CH_3OC_6H_4$	1.30–1.96	2.46–3.00	6.70–7.89
2	$2\text{-}ClC_6H_4$	H	1.36–2.07	2.59–3.33	6.76–8.16
3	$4\text{-}ClC_6H_4$	$3\text{-}ClC_6H_4$	1.27–2.07	2.51–3.07	6.76–7.93
4	$4\text{-}CH_3OC_6H_4$	H	1.16–2.00	2.33–3.00	6.78–7.82
5	$4\text{-}CH_3C_6H_4$	$2,5\text{-}(CH_3O)_2C_6H_3$	1.27–2.07	2.50–3.26	6.50–8.00
6	$4\text{-Cl-}3\text{-}CH_3C_6H_3$	H	1.10–2.03	2.53–3.13	6.73–7.83

TABLE V

Proton magnetic resonance spectra of *cis*-1-(arylsulfonyl)-2-phenylcyclopropanes—V

S. No.	Ar	Cyclopropyl (δ, ppm)			Aryl and arylsulfonyl δ, ppm
		CH_2 (A)	CH_2 (B)	CH	
1	$4\text{-}BrC_6H_4$	1.46–1.74	2.08–2.32	2.52–2.93	7.00–7.60
2	$2\text{-}ClC_6H_4$	1.43–1.93	2.13–2.40	2.48–2.93	6.69–7.56
3	$4\text{-}ClC_6H_4$	1.44–1.79	2.10–2.38	2.46–2.92	7.06–7.38
4	$4\text{-}CH_3OC_6H_4$	1.42–1.72	2.00–2.27	2.52–2.90	6.72–7.36
5	$3\text{-}CH_3C_6H_4$	1.36–1.89	2.03–2.40	2.49–3.00	6.92–7.50
6	$2\text{-}NO_2C_6H_4$	1.46–1.92	2.16–2.44	2.58–3.03	6.59–8.03
7	$4\text{-Cl-}3\text{-}CH_3C_6H_3$	1.31–1.83	2.02–2.40	2.48–2.98	6.81–7.41
8	$5\text{-Cl-}2\text{-}CH_3C_6H_3$	1.36–1.86	2.00–2.30	2.38–3.17	6.73–7.43
9	$C_6H_5CH_2$	1.41–1.86	2.00–2.36	2.43–2.79	7.13–7.65



ties in the regions 1115–1100 and 925–915 (*trans*-configuration),[15] 850–830 (*cis*-configuration),[18] 1330–1305 and 1164–1150 (ν_{SO_2}).[19-21]

The PMR spectra (δ, ppm) of the compounds in the present investigation exhibited complex multiplets in the region 1.40 to 2.40 (methylene), 2.38 to 3.26 (methine) and 6.50 to 8.16 (aryl and arylsulfonyl) (see Tables IV and V).

The configurational assignments can be best made by the analysis of the coupling constants of H_C and H_D of III and V.[13] The earlier assignments of configurations of some 1-(arylsulfonyl)-2-arylcyclopropanes, however, were based on mere analogy of PMR spectral data.[14,15] It was reported that configurations of the cyclopropane derivatives could also be solved by the use of chemical shifts data.[22-24] The substituents in the cyclopropanes generally tend to cause the chemical shifts of ring protons *cis* to them to appear at higher fields than those *trans* to them. In structure V, H_A is having substituents *cis* to it, but H_B has no such *cis*-substituents. As a consequence of this the chemical shifts of H_A is observed at higher fields. There is a considerable difference of chemical shifts between H_A and H_B (see Table V). In structure III, H_A and H_B are having substituents *cis* to them and thus the difference between the chemical shifts of H_A and H_B is remarkably less (see Table IV). Therefore it is clear that the difference in chemical shifts of H_A and H_B is quite distinguishable in V whereas in III, it is almost indistinguishable. Thus, the variation in chemical shifts data can be used as a criterion to assign the configurations of the aryl cyclopropyl sulfones.

EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Microanalyses were performed by Dr. R. D. MacDonald, Australian Microanalytical Service. The IR spectra were recorded on a Perkin-Elmer 257 infrared spectrometer in KBr discs for solids and in liquid films for liquids. The PMR spectra were recorded in dutereochloroform using Varian XL-100 at 100 MHz with TMS as an internal standard.

Reagents. Styrene is obtained commercially and purified by distillation under reduced pressure.

Thiophenols. The arylsulfonyl chlorides were obtained by the chlorosulfonylation of the corresponding hydrocarbons as described by Huntress and Carten.[23] To a mixture of crushed ice and concentrated sulfuric acid the aryl sulfonyl chloride was added with stirring. The Zinc dust was added quickly in portions as rapidly as possible, to the cooled mixture without the rise of temperature above 10°C. The distillate obtained after steam distillation of the mixture was extracted with ether. The product obtained after evaporation of ether was purified. 4-Bromothiophenol; mp 74–76°C, 2-chlorothiophenol; bp 204–206°C/760 mm Hg, 4-chlorothiophenol; mp 52–53°C, 4-methoxythiophenol; bp 225–227°C/760 mm Hg, 4-methylthiophenol; bp 195–196°C/760 mm Hg, 3-methylthiophenol; bp 91–93°C/25 mm Hg, 2-nitrothiophenol; mp 57–58°C, 4-nitrothiophenol; mp 73–74°C, 3,4-dichlorothiophenol; bp 80–81°C/5 mm Hg, 4-chloro-3-methylthiophenol; bp 104–106°C/10 mm Hg, 5-chloro-2-methylthiophenol; bp 126–127°C/30 mm Hg, benzylthiophenol; bp 194–195°C/760 mm Hg.

Aryl chloromethyl sulfides. The aryl chloromethyl sulfides were prepared following the procedure of Francher.[26] A mixture of paraformaldehyde and benzene was taken in a conical flask and to this concentrated hydrochloric acid was added rapidly with stirring. After some time when the mixture was at 40°C the appropriate thiol in benzene was added slowly. The resulting mixture was maintained slightly above 40°C for 2 hrs. After removing the solvent the products were purified. 4-Bromophenyl chloromethyl sulfide; bp 164–165°C/18 mm Hg, 2-chlorophenyl chloromethyl sulfide; bp 148–149°C/15 mm Hg, 4-chlorophenyl chloromethyl sulfide; bp 131–132°C/12 mm Hg, 4-methoxyphenyl chloromethyl sulfide; bp 175–176°C/20 mm Hg, 3-methylphenyl chloromethyl sulfide; bp 124–125°C/ 15 mm Hg, 4-methylphenyl chloromethyl sulfide; bp 158–160°C/20 mm Hg, 2-nitrophenyl chloromethyl sulfide; mp 93–95°C, 4-nitrophenyl chloromethyl sulfide; mp 60–61°C, 4-chloro-3-methylphenyl chloromethyl sulfide; bp 151–152°C/10 mm Hg, 5-chloro-2-methylphenyl chloromethyl sulfide; bp 160–161°C/10 mm Hg, 3,4-dichlorophenyl chloromethyl sulfide; bp 144–145°C/8 mm Hg, benzyl chloromethyl sulfide; bp 120–121°C/15 mm Hg.

The intermediate α,β-unsaturated sulfones were prepared as reported.[27] The trimethylsulfonium iodide was prepared with the procedure of Emeleus and Heal.[28] Anhydrous dimethyl sulfoxide was obtained by refluxing commercial dimethyl sulfoxide over anhydrous barium oxide and then distilling under reduced pressure.

General procedure for the preparation of trans-1-(arylsulfonyl)-2-arylcyclopropanes. In a 100 ml three necked flask equipped with a magnetic stirrer and fitted with a dropping funnel and a calcium chloride guard tube was placed α,β-unsaturated sulfone (0.01 mol), trimethylsulfonium iodide (0.01 mol) and dry dimethyl sulfoxide (20 ml). The contents of the flask were stirred to get a clear solution. Potassium *t*-butoxide (0.01 mol) in dimethyl sulfoxide (20 ml) was added dropwise to this solution, with stirring at room temperature. The reaction mixture was stirred further for 1 hr, diluted with water (300 ml) and stirred until the crude cyclopropyl sulfone was separated. The product was collected, dried and recrystallized from 95% ethanol. The compounds thus obtained are given in Table I.

General procedure for the preparation of cis-1-(arylsulfonyl)-2-phenylcyclopropanes. Styrene (25 ml) was taken in a 250 ml three necked flask equipped with a magnetic stirrer and fitted with a dropping funnel and calcium chloride guard tube. Potassium *t*-butoxide (5 g, 20% excess than 0.025 mol) was added in small portions to the styrene at -5 to -10°C while stirring. The aryl chloromethyl sulfide (0.025 mol) was added drop wise to the reaction mixture. After the complete addition the contents were stirred for 3 hrs and was diluted with water. The oily layer that separated was dried over anhydrous calcium chloride and the *cis*-1-(arylthio)-2-phenylcyclopropane was collected by fractional distillation under reduced pressure. However in some cases the solid separated after removing styrene was purified by recrystallization. The relevant data on the compounds obtained are given in Table II.

The above sulfide (2 g) was dissolved in 20 ml glacial acetic acid and cooled in ice cold temperature. To this 10 ml of 30% hydrogen peroxide was added and the mixture was refluxed for 6 to 10 hrs. The contents were allowed to cool and then poured on to crushed ice with stirring. The product that separated slowly was collected on a Buchner funnel, washed with ice cold water, dried and recrystallized from 2-propanol. The compounds that are synthesized are presented in Table III.

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